

Interaction between diffusion of palm biodiesel and large strain in rubber: Effect on stress-softening during cyclic loading

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In addition to fluctuating multiaxial mechanical loading, many engineering rubber components are exposed to hostile environments such as oil rich environment. In this case, the mechanical response of rubbers is affected by the interaction existed between mechanical loading and diffusion of liquid into the material. The present work attempts to investigate the above interaction and the resulting mechanical response under cyclic loading conditions in nitrile butadiene rubber (NBR) and chloroprene rubber (CR). More precisely, our focus is on the well-known stress-softening (Mullins effect) phenomenon classically observed in rubbers under cyclic loading conditions.

Keywords:

Rubber
Diffusion
Cyclic loading
Stress-softening
Swelling

1. Introduction

In Asian countries such as Malaysia and Indonesia, energy insecurity, increase in energy consumption, and environmental concerns are among the major driving forces for the development of biofuels as partial substitution of petroleum fuels (Jayed et al., 2011). The use of biofuels, derived from plant materials or animal fats, offers an attractive alternative for diesel engines since their use does not require extensive engine modification. If the compatibility of materials in conventional petrodiesel system is well established, the compatibility between biofuels such as palm biodiesel and engineering materials, in particularly rubbers, remain to be explored (Haseeb et al., 2010).

Rubbers are widely used in various applications such as tires, shock absorbers, seals, and gaskets in automotive industry. In a large majority of cases, they are subjected to fluctuating multiaxial loading conditions which can lead to fatigue failure (Mars and Fatemi, 2002; Verron and Andriyana, 2008; Andriyana et al., 2010). In addition, many industrial rubber components are exposed to hostile environments such as acid medium, sea water, or oil rich medium. In this case, the long-term behavior of rubbers are strongly affected by the interaction between mechanical loading and diffusion of liquids. Whenever rubbers are exposed to liquids, one main form of degradation experienced by the materials is swelling which can be described in terms of mass or volume change (Flory, 1953;

Treloar, 1975). During the swelling, liquids penetrate the polymer network and occupy positions among the polymer molecules. Consequently, the macromolecules are forced apart resulting in the swelling of material and to the decrease in its strength since the increase in chain separation yields to the reduction of secondary bonding (Callister, 2007). A number of free swelling tests investigating the diffusion of liquids in stress-free rubbers have been extensively studied (see Treloar, 1975; and references herein). Furthermore, several works investigating the interaction between diffusion of liquids and large deformation in elastomers are available in the literature, namely Baek and Srinivasa (2004), Hong et al. (2008), Soares (2009), Chester and Anand (2010), Duda et al. (2010), Deng and Pence (2010) among others. Nevertheless, no attempts have been made to relate the above interaction with the mechanical response under cyclic loading and the resulting long term fatigue behavior (Zuyev et al., 1964; Magryta et al., 2006; Abu-Abdeen, 2010).

It is well-known that under cyclic loading conditions, rubbers exhibit inelastic responses namely mechanical hysteresis and stress-softening (Verron, 2003). The hysteresis corresponds to the amount of energy loss during a cycle and in the case of dry rubber can be related to either viscoelasticity (Bergström and Boyce, 2000), viscoplasticity (Lion, 1997) and strain-induced crystallization (Trabelsi et al., 2003). Stress-softening is mainly observed during the first cycles. Indeed, for a given strain level in the unloading, the stress decreases with the number of cycle before stabilizes after certain cycles depending on the characteristics of material. This phenomenon, firstly observed by Bouasse and Carrière (1903) then intensively studied by Mullins (1948), is often referred to as

the Mullins effect. Up to this date, no general agreement has been found either on the physical source or on the mechanical modeling of this softening at the microscopic or mesoscopic scales (Dorfmann and Ogden, 2004; Diani et al., 2009).

The present work can be regarded as a first step toward an integrated durability analysis of industrial rubber components exposed simultaneously to fluctuating multiaxial loading and aggressive environments, e.g. oil environment in biofuel systems, during their service. To this end, the understanding of the interaction between diffusion of liquids and large deformation in rubber and the resulting mechanical response under cyclic loading plays an important role. More precisely, our focus is laid on the influence of swelling on stress-softening in rubbers under cyclic loading.

The present paper is organized as follows. In Section 2, the experimental works conducted are discussed including materials, specimen geometry, compression device and the types of test. The experimental results are presented and discussed in Section 3 while concluding remarks are given in Section 4.

2. Experimental program

2.1. Materials

Rubber specimens used in this research are provided by MAKA Engineering Sdn. Bhd., Malaysia. The materials investigated are commercial grade of nitrile butadiene rubber (NBR) and chloroprene rubber (CR) with 60 shore hardness. Biodiesel is prepared by blending palm biodiesel (provided by Am Biofuels Sdn. Bhd., Malaysia) with diesel. The analysis report of the palm biodiesel investigated is shown in Table 1. The immersion tests conducted are immersion in B0 (100% diesel), B25 (blend of 25% of biodiesel and 75% of diesel), B75 (blend of 75% of biodiesel and 25% of diesel) and B100 (100% biodiesel). All blend percentages are given in volume basis.

Table 1
Properties of B100 palm biodiesel.

Test	Unit	Methods	Results
Ester content	% (m/m)	EN 14103	96.9
Density at 15 °C	kg/m ³	EN ISO 12185	875.9
Viscosity at 40 °C	mm ² /s	EN ISO 3104	4.667
Flash point	°C	EN ISO 3679	168
Cetane number	–	EN ISO 5165	69.7
Water content	mg/kg	EN ISO 12937	155
Acid value	mgKOH/g	EN ISO 3679	0.38
Methanol content	% (m/m)	EN 14110	<0.01
Monoglyceride content	% (m/m)	EN 14105	0.67
Diglyceride content	% (m/m)	EN 14105	0.2
Triglyceride content	% (m/m)	EN 14105	0.2
Total glycerine	% (m/m)	EN 14105	0.25

2.2. Specimen geometry and compression device

In order to investigate the interaction between diffusion and large deformation in rubbers and its resulting mechanical response under cyclic loading condition, an annular rubber specimen having height, outer diameter, and wall thickness of 10 mm, 50 mm, and 6 mm, respectively is considered. The specimens are placed in a home-made compression device as illustrated in Fig. 1. As depicted in this figure, four stainless steel plates are arranged successively and separated by three sets of spacer bar having different heights: 8 mm, 9 mm, and 9.8 mm. Four rubber specimens are placed in each level. The plates are tightened using bolts and nuts until they are uniformly in contact with the respective spacer bar. Since the height of the rubber specimen is 10 mm, the above arrangement allows the application of different engineering pre-compressive strains to the specimen: 2%, 10% and 20%. The device containing rubber specimens is subsequently immersed into different palm biodiesel blends for durations of 30 and 90 days. The details of the immersion tests is given in Table 2. In order to determine the swelling level (change of volume), the volume of the specimen is measured before

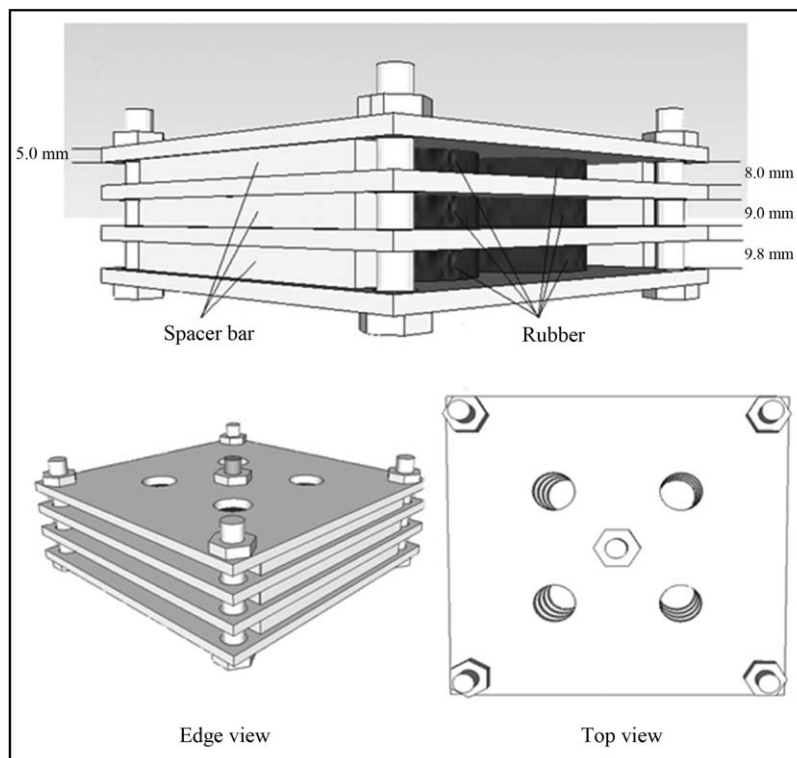


Fig. 1. Home-made compression device for the observation of the coupling between diffusion and large deformation in rubbers (Chai et al., 2011).

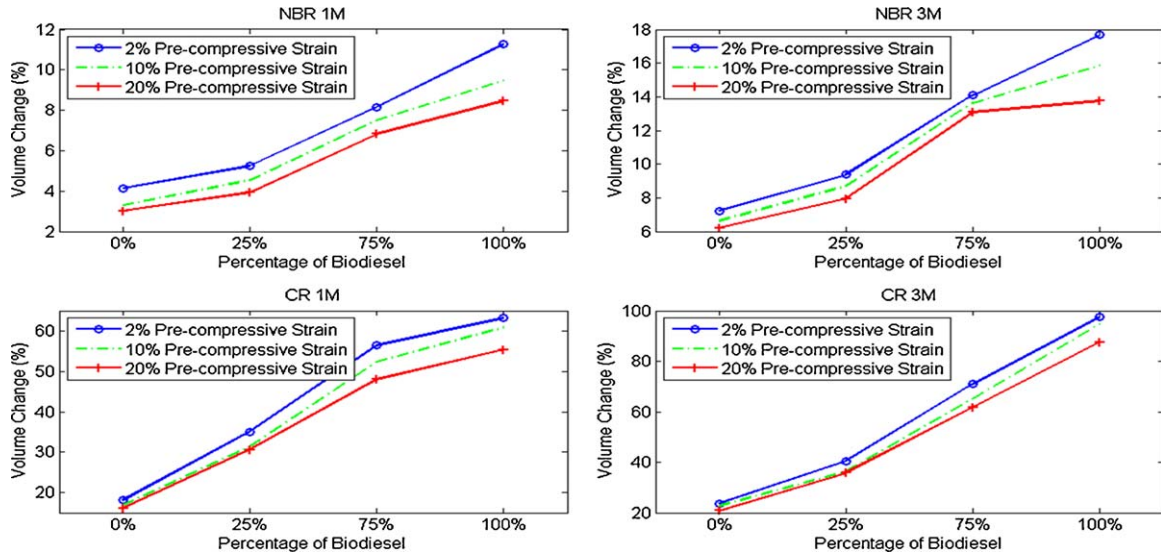


Fig. 2. Volume changes of NBR and CR at different compressive strains after 1 month (1M) and 3 months (3M) of immersion in different biodiesel blends.

Table 2
Immersion tests.

Biodiesel blend	Level of pre-compressive strain (%)	Immersion duration
B0	2/10/20	30/90 days
B25	2/10/20	30/90 days
B75	2/10/20	30/90 days
B100	2/10/20	30/90 days

and after the immersion. The test procedure for the measurement of volume change can be summarized as followed:

1. Before the immersion, the weight of the rubber specimen is measured in air and in distilled water. The specimen is then quickly dipped into alcohol and blotted dry with filter paper.
2. After weight measurement, the rubber specimens are placed in sequence on the compression plates. Grease is applied on the surface of the specimens that are in contact with the compression plate to avoid bulging of the specimens. Thereby ensuring the specimens to be in a simple uniaxial compressive stress state.

3. Bolts and nuts are used to tighten the compression device until the compression plates are uniformly in contact with the spacers. The device containing rubber specimens is subsequently immersed completely into different biodiesel blends for 30 or 90 days.
4. At the end of each immersion period, the specimens are removed from the compression device and quickly dipped into acetone; it is then cleaned with filter paper to remove the excess oil. The specimens are left for 30 min to allow for recovery before any measurement is made after immersion.
5. Step 1 is repeated to measure the weight of rubber specimen after immersion.

The percentage of volume change is calculated using the following relation (Trakarnpruk and Porntangitlikit, 2008):

$$= \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100 \quad (1)$$

where M_1 and M_2 are the mass in air (g) before and after immersion while M_3 and M_4 are mass in water (g) before and after immersion.

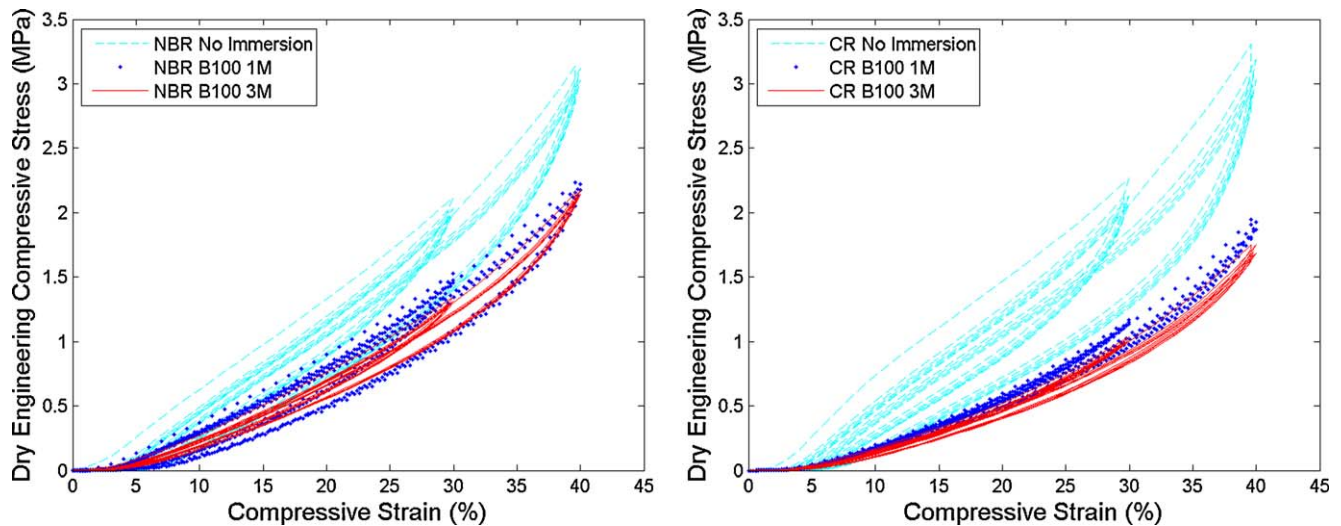


Fig. 3. Stress-strain curves of NBR (left) and CR (right) under cyclic loading conditions at dry states (without immersion) and after 1 month (1M) and 3 months (3M) of immersion in B100. Results correspond to pre-compressive strain of 2%.

For each biodiesel content, pre-compressive strain and immersion duration, at least four specimens are used in the measurement of volume change.

Remark 2.1. In practice, the 2% pre-compressive strain is so small that its effect on the macroscopic mechanical response is negligible. Nevertheless, this level of strain is retained to represent initially stress-free condition while ensuring that the diffusion occurs only along radial direction. The details about the compression device is given in Chai et al. (2011).

2.3. Mechanical testing

After each period of immersion, the mechanical response of the swollen rubbers under cyclic loading condition is investigated. For this purpose, cyclic tests using Instron 5500 uniaxial test machine equipped with 10 kN load cell at room temperature are conducted. To ensure uniform displacement control on the specimens, circular compression plates are attached to the machine. The experimental setup is connected to a computer to record the experimental data. All tests are conducted in compression at a constant displacement rate of 0.1 mm/s to avoid excessive increase in the temperature of the specimens, i.e. thermal effects are not considered in the present study. The specimens are subjected to cyclic compressive loading at two different maximum engineering compressive strains: 30% and 40% of 6 cycles each.

Remark 2.2. It is important to remember that the word “strain” used in this study corresponds to the engineering strain defined with respect to the *unswollen-unstrained* configuration.

3. Results and discussion

3.1. Change in volume

Fig. 2 presents the volume changes experienced by NBR and CR for different contents of biodiesel, different durations of immersion and different pre-compressive strains. The graphs clearly show the increase of volume in both materials after immersion. In general, it is found that the volume increases with biodiesel content and duration of immersion. As indicated in this figure, CR shows significantly higher change in volume than NBR. Indeed, it is observed that the volume change ranges between 18–98% and 3–18% for CR and NBR respectively.

The pre-compressive strain appears to give restriction to the diffusion of liquid into rubber. Indeed, as the pre-compressive strain increases, the resulting volume change decreases. The corresponding results can be explained by the fact that as higher pre-compressive strain is introduced, the initial effective area provided by the rubber specimens for diffusion of liquid to occur becomes smaller. Moreover, as evoked by Treloar (1975), the presence of compressive stress in the material reduces diffusion since the hydrostatic part of this stress state is positive. In the next subsection, only results that correspond to 2% pre-compressive strain are presented since the pre-compressive strain of 2% yields to the highest level of swelling.

3.2. Stress-softening

The stress-strain responses under cyclic compressive loading conditions at two different maximum compressive strains of previously non-immersed (dry) and immersed (swollen) NBR and CR are depicted in Fig. 3. For each value of maximum compressive strain, the specimen experiences six cycles of loading. It is important to highlight that the stress given in this figure is expressed with respect to the *unswollen-unstrained* configuration (dry cross-section). As indicated in this figure, no significant difference in the

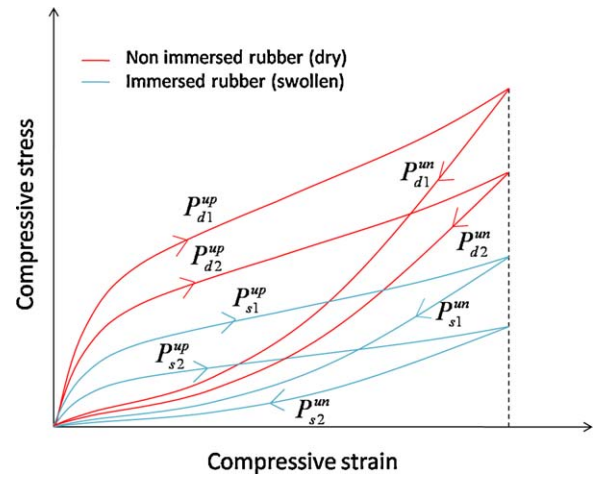


Fig. 4. Illustration of two first cycles stress-strain curve of previously non-immersed (dry) and immersed (swollen) rubbers under cyclic loading.

nature of stress-strain behavior between dry and swollen rubbers is observed. Nevertheless, for a given strain, lower stresses are recorded for swollen rubbers; and CR exhibits larger stress drop than NBR. In either dry or swollen state, NBR and CR exhibit inelastic responses, i.e. mechanical hysteresis and stress-softening. The former, characterized by the difference between uploading and unloading paths during one cycle, decreases with loading cycle and stabilizes after five cycles. Moreover, the mechanical hysteresis exhibited by dry CR is slightly larger than that of dry NBR. For both materials, the presence of liquids appears to decrease the size of hysteresis loop. The latter, i.e. stress-softening characterized by the difference in stress during the first few uploading, disappears after five cycles.

Before proceeding further with the nature of stress-softening in the presence of biodiesels, it is important to recall the difference between the decrease in stress associated with the decrease in strength of rubber and the decrease in stress associated with stress-softening. The former compares the stress level during the first uploading between dry rubber and swollen rubber. The latter compares the stress level during the first and the second uploadings in one rubber (either dry or swollen). To characterize the former and the latter, we use the terms *stress drop* and *stress-softening* respectively defined by (see Fig. 4).

$$\text{Stress drop} = \frac{P_{d1}^{up} - P_{s1}^{up}}{P_{d1}^{up}} \quad (2)$$

$$\text{Stress - softening (dry)} = \frac{P_{d1}^{up} - P_{d2}^{up}}{P_{d1}^{up}};$$

$$\text{Stress - softening (swollen)} = \frac{P_{s1}^{up} - P_{s2}^{up}}{P_{s1}^{up}} \quad (3)$$

where P_{d1}^{up} is the stress in dry rubber during uploading of the first cycle, P_{d2}^{up} is the stress in dry rubber during uploading of the second cycle, P_{s1}^{up} is the stress in swollen rubber during uploading of the first cycle and P_{s2}^{up} is the stress in swollen rubber during uploading of the second cycle. The use of Eq. (3) for the definition of stress-softening implies that we only focus on the softening which occurs between the first and the second uploading, i.e. further stress-softening after the second uploading is not considered. In the next paragraph, the evolution of stress drop and stress-softening in the presence of biodiesel is discussed with emphasis being given in the latter. Furthermore, the next discussion is restricted only to results related to

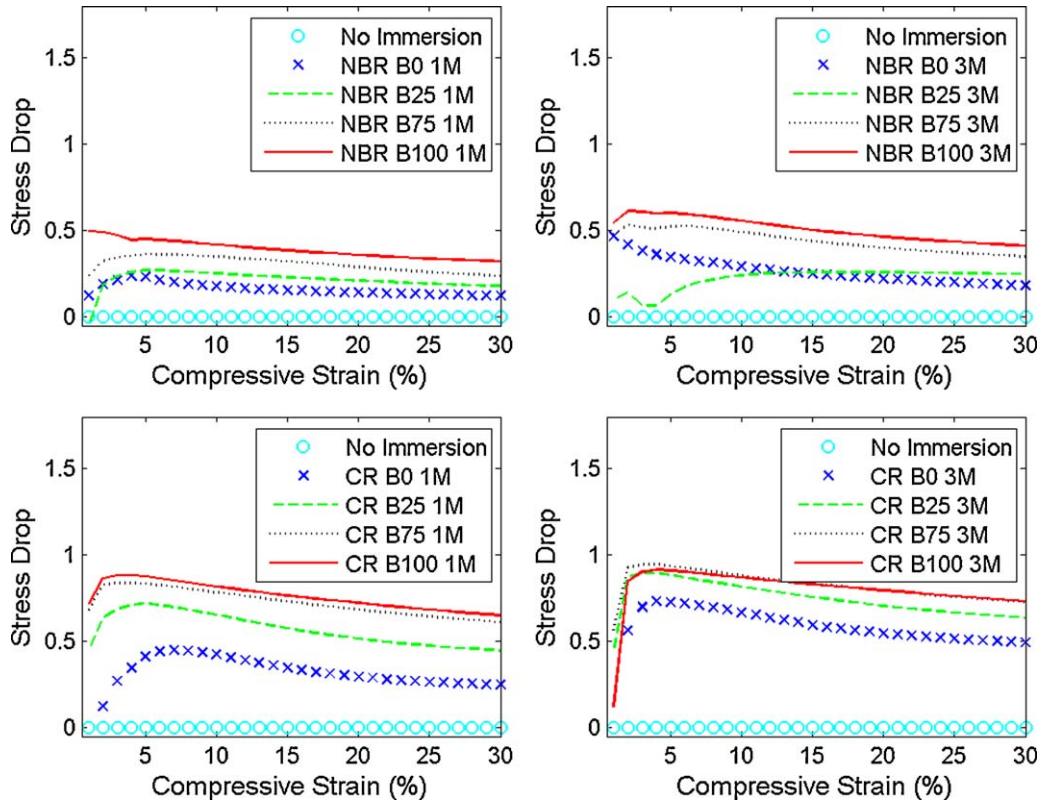


Fig. 5. Stress drop in NBR and CR previously immersed in various biodiesels for two different durations of immersion: 1 month (1M) and 3 months (3M). Results correspond to pre-compressive strain of 2%.

maximum applied cyclic compressive strain of 30% since the data at larger strains shows similar trend.

Remark 3.3. In order to compare the stress drop and stress-softening of the materials in different biodiesels and different immersion durations, it is important to remember that for swollen rubbers, the stresses P_{s1}^{up} and P_{s2}^{up} have to be expressed with respect to the *unswollen-unstrained* configuration.

The stress drop exhibited by NBR and CR are shown in Fig. 5. Note that, the stress drop in dry (non-immersed) rubbers is zero by definition. As depicted in this figure, both NBR and CR experience a stress drop in the presence of biodiesels. Moreover, in the range of 5%–30% strain, the stress drop appears to be decreasing slightly with the applied strain. However, the corresponding drop

increases with the biodiesel content and duration of immersion, i.e. the strength of rubber decreases further with the increase of biodiesel content and duration of immersion. For given biodiesel content and duration of immersion, CR exhibits larger stress drop than NBR. The high level of swelling experienced by CR as shown in Fig. 2 contributes significantly to the decrease of its strength.

Concerning stress-softening, it generally decreases as the strain level approaches the maximum strain previously endured by the material as classically observed in rubber under cyclic loading conditions (Diani et al., 2009). Unlike the stress drop, an opposite trend is found in stress-softening, i.e. the presence of liquids decreases stress-softening as shown in Figs. 6–10. Initially, at dry state, CR exhibits slightly higher level of stress-softening than NBR as depicted in Fig. 6. Nevertheless, as the material is immersed for

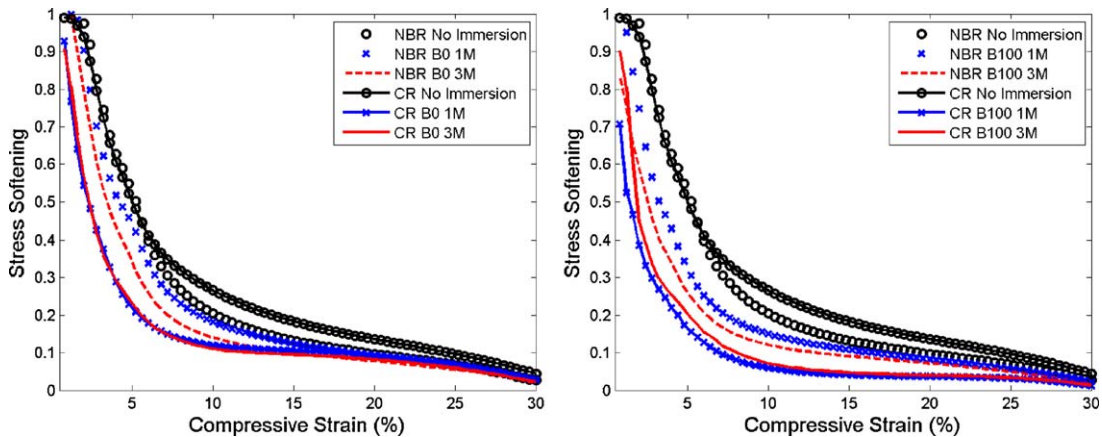


Fig. 6. Stress-softening in NBR and CR previously immersed in B0 (left) and B100 (right) for two different durations of immersion: 1 month (1M) and 3 months (3M). Results correspond to pre-compressive strain of 2%.

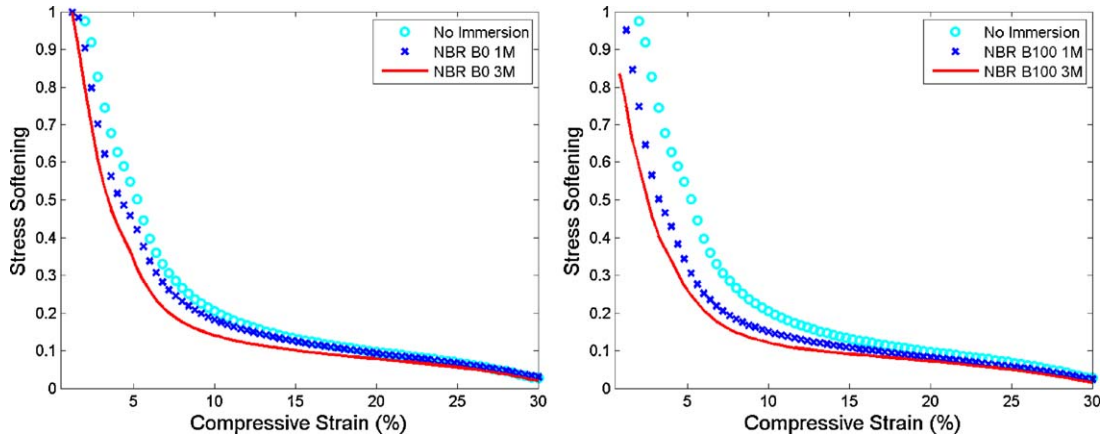


Fig. 7. Stress-softening in NBR previously immersed in B0 (left) and B100 (right) for two different durations of immersion: 1 month (1M) and 3 months (3M). Results correspond to pre-compressive strain of 2%.

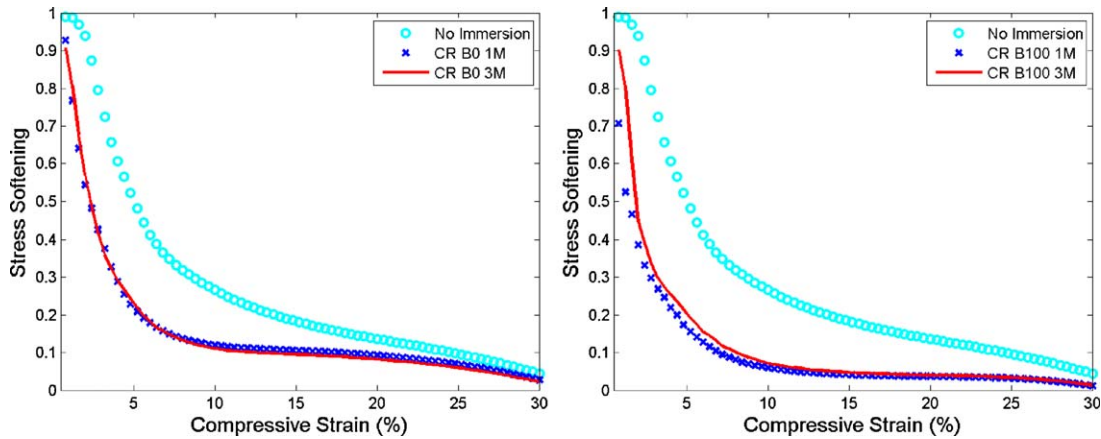


Fig. 8. Stress-softening in CR previously immersed in B0 (left) and B100 (right) for two different durations of immersion: 1 month (1M) and 3 months (3M). Results correspond to pre-compressive strain of 2%.

1 month in either B0 or B100, the stress-softening decreases significantly in CR and becomes lower than that of NBR. In NBR, for a compressive strain of 10%, the amount of stress-softening drops from 20% at dry state to 18% and 15% at swollen state (immersed in B0 and B100 respectively for 1 month) as presented in Fig. 7. Increasing the duration of immersion from 1 month to 3 months yields to a further decrease of stress-softening to around 15% and

12% in B0 and B100 respectively. Referring to Fig. 2, this corresponds to the swelling level of 11% and 18% respectively.

In the case of CR, at applied compressive strain of 10%, the amount of stress-softening changes from 28% for dry state to only 12% and 8% when it is immersed respectively in B0 and B100 for 1 month as shown in Fig. 8. Note that in the latter condition, the volume change exhibited by the material is around 18% and 64%

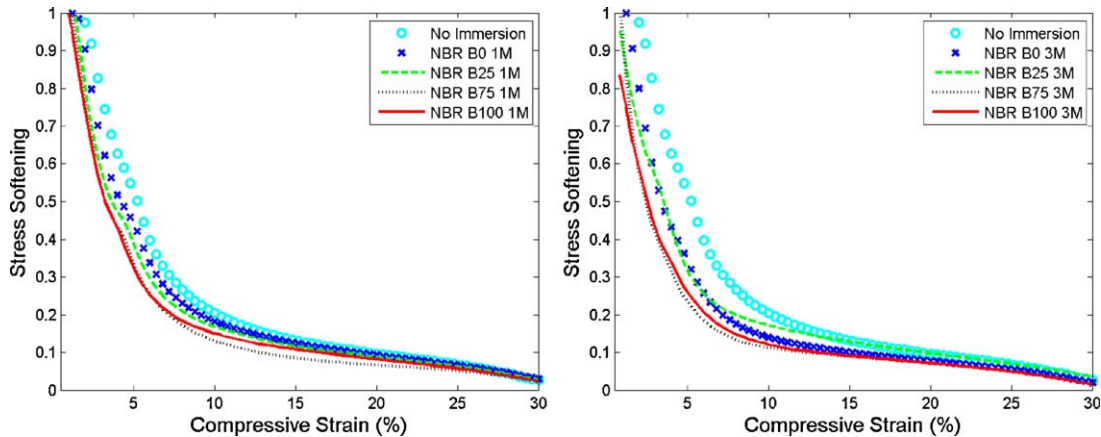


Fig. 9. Stress-softening in NBR previously immersed in various biodiesels for two different durations of immersion: 1 month (1M) (left) and 3 months (3M) (right). Results correspond to pre-compressive strain of 2%.

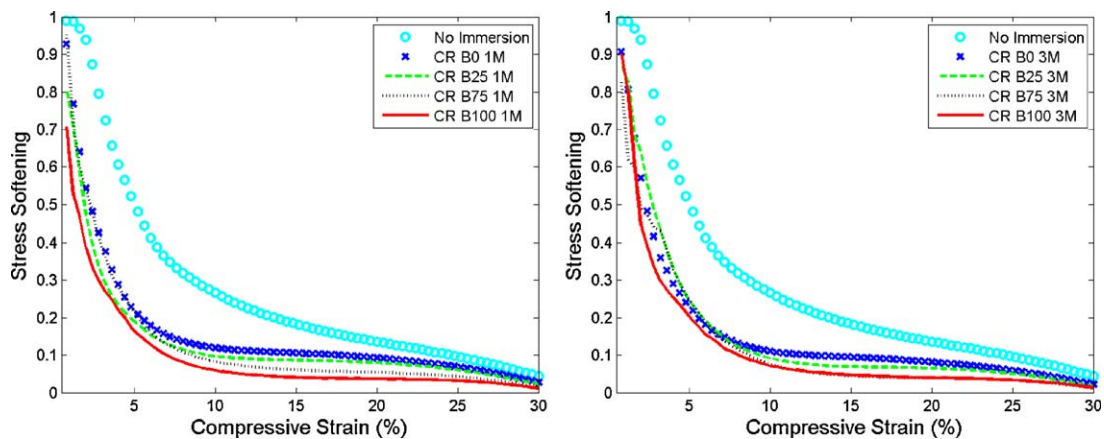


Fig. 10. Stress-softening in CR previously immersed in various biodiesels for two different durations of immersion: 1 month (1M) (left) and 3 months (3M) (right). Results correspond to pre-compressive strain of 2%.

respectively (see Figure 2). Increasing the duration of immersion from 1 month to 3 months yields to a significant increase in the volume change to around 24% and 90% in B0 and B100 respectively. However, the level of stress-softening appears to be unaffected by the corresponding further increase in swelling. Finally, the effect of biodiesel content on stress-softening in NBR and CR is presented in Fig. 9 and Fig. 10. In these figures, it is found that for both materials, the increase in the content of biodiesel decreases the level of stress-softening.

To close the paper, it is to note that all inelastic phenomena, e.g. stress-softening and mechanical hysteresis, in rubbers resulting from cyclic loading conditions appear to diminish significantly due to the presence of liquids, i.e. the macroscopic mechanical response of swollen rubbers approaches the response of hyperelastic materials. Nevertheless, the physical mechanism by which the presence of liquids modify the mechanical response under the above loading condition remains unknown.

4. Conclusion

In this work, the interaction between diffusion of liquids and large strain in rubber, and its resulting mechanical response under cyclic loading conditions were investigated. Two types of rubber were considered: NBR and CR. For given biodiesel content and duration of exposure, it was found that CR experienced higher changes in volume than NBR. Pre-compressive strain gave restriction for diffusion of liquids. Moreover, for a given duration of immersion, higher content of biodiesel yields to higher level of swelling in both rubbers.

Under cyclic loading conditions, inelastic phenomena in swollen rubbers appeared to be significantly smaller than that of dry rubber, i.e. smaller stress-softening and mechanical hysteresis were recorded. The increase in the content of biodiesel decreased further the aforementioned phenomena. More extensive studies on the physical mechanism by which the presence of liquids modify the mechanical response under cyclic loading condition are needed in the near future.

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